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PATENT COOPERATION TREATY

539,881

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference LU6076	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/EP 03/14265	International filing date (day/month/year) 16.12.2003	Priority date (day/month/year) 16.12.2002
International Patent Classification (IPC) or both national classification and IPC C08F110/06		
Applicant BASELL POLYOLEFINE GMBH et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.


2. This REPORT consists of a total of 6 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 4 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the opinion
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 07.07.2004	Date of completion of this report 03.08.2005
Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized Officer Parry, J Telephone No. +31 70 340-1032

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP 03/14265

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, Pages

1-19 as originally filed

Claims, Numbers

1-8 filed with telefax on 01.07.2005

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☒ the claims, Nos.: 9,10
- ☐ the drawings, sheets:

5. ☒ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

see separate sheet

6. Additional observations, if necessary:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/EP 03/14265

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes: Claims	1-10.
	No: Claims	
Inventive step (IS)	Yes: Claims	
	No: Claims	1-10.
Industrial applicability (IA)	Yes: Claims	1-10.
	No: Claims	

2. Citations and explanations

see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP 03/14265

Re Item I

Basis of the opinion

1. Claim 1: the amendment "branched alkyl radical having 3-10 carbon atoms" appears to have no basis in the application as originally filed. Although the correction to a number greater than 2 is obvious for a branched alkyl, that that number might be corrected to "3", as opposed to 4, 5, or 6 and so on, in order to form the lower range 3-10 is not obvious (Art. 34 PCT). This amendment has therefore been ignored (see Box VIII). The other amendments are allowable.

Re Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

The following documents (D1-D3) will be referred to (see the ISR for additional relevant passages):

D1: DATABASE CHEMABS [Online]
CHEMICAL ABSTRACTS SERVICE, COLUMBUS,
OHIO, US;
ISHIGAKI, SATOSHI ET AL: "Metallocene
catalysts solubilized in hydrocarbon
solvents and manufacture of polyolefins"
XP002277233

D2: WO 98/01481 A (SCHWEIER GUENTHER ; BASF AG
(DE); FISCHER DAVID (DE); MOLL ULRICH
(DE)) 15 January 1998 (1998-01-15)

D3: EP 0 582 480 A

1. D1, considered the closest prior art, describes insoluble metallocenes (bridged or non-bridged according to claim 1 therein) which are dissolved in hydrocarbon solvents with $i\text{Bu}_3\text{Al}$ and then added to MAO/silica. Example 1 (para 57-58) of the translation of the corresponding Japanese patent application shows that these processes, as applied to a non-bridged metallocene and employing MAO/silica with $i\text{Bu}_3\text{Al}$ (as required in present

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP 03/14265

claim 1), lead to no reactor fouling. Example 4 (para 63) similarly uses a substituted metallocene $\text{Me}_2\text{Si}-(2\text{-Me},4\text{-Ph- indenyl})\text{ZrCl}_2$, which falls both under claim 1 therein and present claim 1, but with a borate cocatalyst instead of MAO. The examples disclose both homo-ethylene polymerisation and homo-propylene polymerisation. The skilled person would seriously consider working under the entire range of claim 1 of D1 with respect to examples therein, including employing such compounds as found in example 4 of D1 with cocatalysts as used in example 1 therein. Hence the combination of the hints provided in examples 1 and 4 of D1 with respect to claim 1 of D1 would have destroyed the novelty of claims 1-8 if an evaporation step as found in present claim 1 (incorporated from old claim 5) were absent. This is because, although in claim 1 of D1 the term "alumoxane is removed" is employed (which, presumably, by reference to the Chemical Abstracts abstract, means "alumoxane is excluded"), example 1 therein does indeed use alumoxane and results in no reactor fouling. It seems the gist of the invention of D1 from the examples is not to use alumoxane with the aliphatic solvents of claim 1, and this claim actually reads "alumoxane is excluded in aliphatic hydrocarbons". Thus example 1 using alumoxane in toluene (para 57-58) shows no reactor fouling, whereas the repeat experiment using alumoxane in hexane (comparison 2, para 67) shows reactor fouling. There is no expression of the solvent to be used in present claim 1. D1 differs therefore from present claim 1 in that an evaporation step is absent. The technical effect of this step has not been demonstrated over D1. Any such technical effect would have had to be demonstrated by employing throughout identical conditions to those found in D1 save for the evaporation step in the catalyst preparation. The problem to be solved is thus only to provide alternative processes for the preparation of catalysts. This cannot be considered inventive as said evaporation step is disclosed in D2. D2 discloses metallocene catalysts of the present examples premixed with MAO and added to (silica + MAO). The product is dried by evaporation. MAO itself contains occluded Me_3Al , but not occluded branched alkyl analogues as specified in new (present) claim 1. The skilled person would thus consider it a normal option to combine documents D1 and D2 to solve the present problem.

2. Note that in the absence of any demonstrated technical effect, it would have been trivial to employ iBu_2AlH of present claim 1 (as used in D3) instead of the iBu_3Al of D1.

Re Item VIII

Certain observations on the international application

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP 03/14265

The following objections are made under Art. 6 (PCT):

1. Claim 1: R7, R8 and R9 cannot all be H or H plus alkoxy if formula VIII is to represent an organometallic compound.

2. Claim 2: (i) "active hydrogen" is unclear. Since the nature of the activity has not been defined with respect to a point of reference (ie, what is being protonated?), one cannot ascertain what sort of hydrogen centres would fall under this definition. The term should have been specified according to p.7, l.9-12, not merely according to p.7, l.9-10.

(ii) "...so that essentially.." describes a "result to be achieved" (PCT GL Ch.-III,4.7). The amount of aluminoxane should have been specified according to p.8, l.17-18.

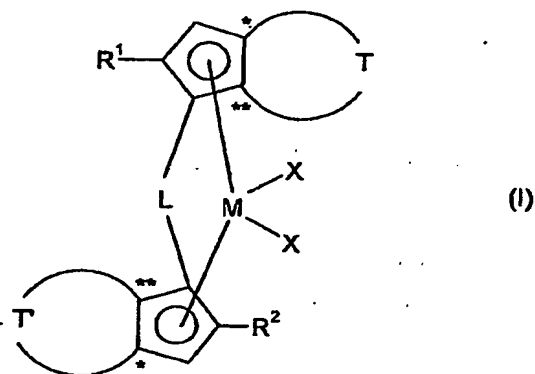
3. Claim 3: a "branched alkyl" cannot comprise 1-2 carbon atoms.

4. The subject matter related to the above-mentioned objections 1-3 will be ignored with respect to the considerations under Box V, since being unclear, it cannot be considered limiting for the scope of the claims.

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We claim:

1. A process for preparing a catalyst solid for olefin polymerization, comprising a finely divided support, an aluminoxane and a metallocene compound, which comprises
- firstly combining the finely divided support with the aluminoxane and subsequently
 - adding the reaction product of a metallocene compound of the formula (I),



where

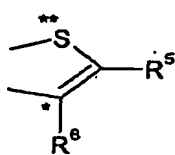
M is zirconium, hafnium or titanium,

X are identical or different and are each, independently of one another, hydrogen or halogen or a group -R, -OR, -OSO₂CF₃, -OCOR, -SR, -NR₂ or -PR₂, where R is linear or branched C₁-C₂₀-alkyl, C₃-C₂₀-cycloalkyl which may bear one or more C₁-C₁₀-alkyl radicals as substituents, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl and may contain one or more heteroatoms from groups 13 - 17 of the Periodic Table of the Elements or one or more unsaturated bonds, with the two radicals X also being able to be joined to one another,

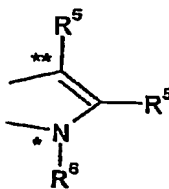
L is a divalent bridging group selected from the group consisting of C₁-C₂₀-alkylidene, C₃-C₂₀-cycloalkylidene, C₆-C₂₀-arylidene, C₇-C₂₀-alkylarylidene and C₇-C₂₀-arylalkylidene radicals which may contain heteroatoms from groups 13 - 17 of the Periodic Table of the Elements or is a silylidene group having up to 5 silicon atoms,

R^1 and R^2 are identical or different and are each, independently of one another, hydrogen or linear or branched C_1 - C_{20} -alkyl or C_3 - C_{20} -cycloalkyl which may bear one or more C_1 - C_{10} -alkyl radicals as substituents, C_6 - C_{20} -aryl, C_7 - C_{40} -alkylaryl or C_7 - C_{40} -arylalkyl and may contain one or more heteroatoms from groups 13 - 17 of the Periodic Table of the Elements or one or more unsaturated bonds,

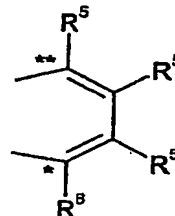
T and T' are divalent groups of the formulae (II), (III), (IV), (V), (VI) or (VII),



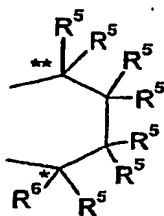
(II)



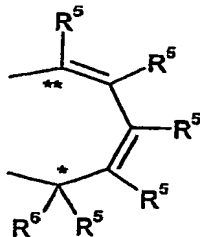
(III)



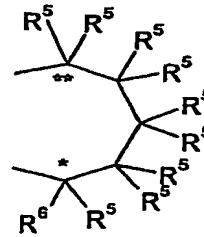
(IV)



(V)



(VI)



(VII)

where

the atoms denoted by the symbols * and ** are in each case joined to the atoms of the compound of the formula (I) which are denoted by the same symbol, and

R^5 and R^6 are identical or different and are each, independently of one another, hydrogen or halogen or linear or branched C_1 - C_{20} -alkyl or C_3 - C_{20} -cycloalkyl which may bear one or more C_1 - C_{10} -alkyl radicals as substituents, C_6 - C_{40} -aryl, C_7 - C_{40} -alkylaryl or C_7 - C_{40} -arylalkyl and may contain one or more heteroatoms from groups 13 - 17 of the Periodic Table of the Elements or one or more unsaturated bonds or two radicals R^5 or R^5 and R^6 are joined to one another to form a saturated or unsaturated C_3 - C_{20} ring,

with at least one organometallic compound of the formula (VIII)



5 where

M^1 is an alkali metal, an alkaline earth metal or a metal of group 13 of the Periodic Table,

10 R^7 is hydrogen, C_1 - C_{10} -alkyl, C_3 - C_{10} -cycloalkyl, C_6 - C_{15} -aryl, alkylaryl or arylalkyl each having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part,

15 R^8 and R^9 are each hydrogen, halogen, C_1 - C_{10} -alkyl, C_3 - C_{10} -cycloalkyl, C_6 - C_{15} -aryl, alkylaryl, arylalkyl or alkoxy each having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part,

r is an integer from 1 to 3

20 and

s and t are integers from 0 to 2, where the sum $r+s+t$ corresponds to the valence of M^1 , and

25 wherein the organometallic compounds of the formula (VIII) which are used have at least one branched alkyl radical having from 3 to 10 carbon atoms or cycloalkyl radical having from 3 to 10 carbon atoms,

30 to the modified support, wherein each of the steps a) and b) is carried out in suspension and the suspension medium is removed by evaporation after step b).

2. A process for preparing a catalyst solid for olefin polymerization as claimed in claim 1, wherein the support used bears functional groups containing active hydrogen and the support and the amount of aluminosilane are selected so that essentially the total amount of
35 the aluminosilane used has reacted with the functional groups of the support containing active hydrogen.

3. A process for preparing a catalyst solid for olefin polymerization as claimed in claim 1 or 2, wherein the organometallic compound of the formula (VIII) which is used is
40 triisobutylaluminum, diisobutylaluminum hydride or a mixture of the two compounds.

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EP0314265

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23

4. A catalyst solid obtainable by a process as claimed in any of claims 1 to 3.
5. A catalyst system for the polymerization of olefins, comprising a catalyst solid as claimed in claim 4.
- 5 6. The use of a catalyst solid prepared as claimed in any of claims 1 to 3 for the polymerization of olefins.
7. The use of a catalyst system as claimed in claim 5 for the polymerization of olefins.
- 10 8. A process for the polymerization of olefins using a catalyst system as claimed in claim 5.

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